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(19) (CA) **CANADIAN PATENT** (12)

(54) Recovery of 1-Butene from C₄-Hydrocarbon
Mixtures Containing 2-Butenes

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Abstract of the Disclosure: 1-Butene is recovered from a C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene by catalytic isomerization of the 2-butenes to 1-butene at elevated temperatures and isomerization of the 1-butene, by a process in which the said isomerization is carried out in the presence of an acidic catalyst at from 150 to 500°C, the isomerization mixture obtained from the isomerization zone is fed into a distillation zone, 1-butene is taken off at the top of the distillation zone, a fraction containing 2-butenes is taken off in the lower third of the distillation zone and fed into the isomerization zone, and the starting C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene is fed to the distillation zone and/or the isomerization zone.

We claim:-

1. A process for recovering 1-butene from a C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene by catalytic isomerization of the 2-butenes to 1-butene at elevated temperatures and isolation of the 1-butene, wherein the said isomerization is carried out in the presence of an acidic catalyst at from 150 to 500°C, the isomerization mixture obtained from the isomerization zone is fed into a distillation zone, 1-butene is taken off at the top of the distillation zone, a fraction containing 2-butenes is taken off in the lower third of the distillation zone and fed into the isomerization zone, and the starting C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene is fed to the distillation zone and/or the isomerization zone.
2. A process as claimed in claim 1, wherein the fraction which contains 2-butenes and is taken off from the lower third of the distillation zone contains from 1 to 15% by weight of 1-butene.
3. A process as claimed in claim 1, wherein the starting C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene is obtained by extractive distillation with the aid of a selective solvent, from a C₄-hydrocarbon mixture which contains butanes and 2-butenes and may or may not contain 1-butene.
4. A process as claimed in claim 1, wherein a solid catalyst is used, and regeneration of this catalyst is carried out by treatment with phosphoric acid.
5. A process as claimed in claim 1, wherein a solid catalyst is used, and regeneration of this catalyst is carried out by combustion with an oxygen-containing gas.

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Recovery of 1-butene from C₄-hydrocarbon mixtures
containing 2-butenes

The present invention relates to a process for recovering 1-butene from C₄-hydrocarbon mixtures containing 2-butenes by catalytic isomerization of the 2-butenes to 1-butene.

U.S. Patent 2,921,103 has disclosed that 2-butenes can be isomerized at 610°C over a chromium oxide/aluminum oxide catalyst to give 1-butene, steam being used as a diluent. However, in spite of the use of steam as a diluent, a time-on-stream of the catalyst of only 10 - 100 hours is achieved in this process. If the conventional process is carried out without the addition of steam, the time-on-stream is no longer than 2 hours. The catalyst has to be regenerated frequently and high dilution with steam is required, so that the process is very labor-intensive and energy-consuming.

It is an object of the present invention to provide a process for recovering 1-butene from a C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene by catalytic isomerization of the 2-butenes to 1-butene, the process being less labor-intensive and energy-consuming than the conventional processes.

We have found that this and other objects and advantages are achieved, in accordance with the invention, by a process for recovering 1-butene from a C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene by catalytic isomerization of the 2-butenes to 1-butene at elevated temperatures and isolation of the 1-butene, wherein the said isomerization is carried out in the presence of an acidic catalyst at from 150 to 500°C, the isomerization mixture obtained from the isomerization zone is fed into a distillation zone, 1-butene is taken off at the top of the distillation zone, a fraction containing 2-butenes is taken off in the lower third of the



distillation zone and fed into the isomerization zone, and the starting C_4 -hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene is fed to the distillation zone and/or the isomerization zone.

5 Even without the addition of steam, a substantially longer time-on-stream of the isomerization catalyst is achieved in the novel process than in the conventional one. Moreover, because it is not necessary to add steam and the isomerization is carried out at a relatively low
10 temperature, the process does not require expensive apparatus and has a low energy consumption. It is surprising that the novel process can be carried out in an extremely economical manner and that the specific energy requirement for the recovery of 1-butene can be kept low, because the
15 isomerization equilibrium between the 2-butenes and 1-butene is shifted in favor of the 2-butenes when the temperature is decreased. It is also surprising that, even without the addition of steam, the formation of cracked products and products of skeleton isomerization of the
20 butenes in the isomerization stage is at such a low level that further purification stages for separating off such crack products and skeleton isomerization products can be dispensed with and 1-butene obtained in high yield.

 The C_4 -hydrocarbon mixtures which contain 2-
25 butenes and may or may not contain 1-butene and are used for the novel process generally have a content of 2-butenes and, where relevant, 1-butene of from 70 to 100, as a rule from 80 to 100, in particular from 90 to 100, % by weight. 2-Butene can be present as cis-2-butene or
30 trans-2-butene, but as a rule the starting C_4 -hydrocarbon mixture contains cis-2-butene and trans-2-butene. In addition to containing the 2-butenes, the said hydrocarbon mixture can contain as much as 90, as a rule from 1 to 70, in particular from 1 to 60, % by weight of 1-butene.

35 The C_4 -hydrocarbon mixtures which contain 2-butenes and may or may not contain 1-butene are advantageously obtained by extractive distillation of a C_4 -hydro-

carbon mixture which contains butanes, such as isobutane and n-butane, and 2-butenes and may or may not contain 1-butene, a selective solvent being used. Advantageously, the butanes, which are less soluble in the selective solvent, are separated off as a top product of the extractive distillation, while at the same time an extract containing the butenes and the selective solvent is taken off from the said distillation. The extract obtained is then freed from the selective solvent to give a C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene and can be used as a starting mixture for the novel process. Examples of suitable selective solvents for separating the butanes and butenes are carboxamides, such as dimethylformamide, diethylformamide, dimethylacetamide or N-formylmorpholine, acetonitrile, furfural, N-methylpyrrolidone, butyrolactone and acetone and mixtures of these with water. N-Methylpyrrolidone is particularly advantageously used as the selective solvent.

For the process according to the invention, the starting C₄-hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene can be fed to the distillation zone and/or the isomerization zone. The starting C₄-hydrocarbon mixture is advantageously fed to the distillation zone, for example to the lower third, or preferably the middle third, of this zone, if, in addition to containing 2-butenes, the said mixture contains 1-butene, for example in a concentration which is higher than the 1-butene concentration established in the isomerization zone. On the other hand, if the starting C₄-hydrocarbon mixture has a high content of 2-butenes, for example not less than 90, as a rule not less than 92, in particular not less than 95, % by weight, the said mixture is generally fed to the bottom of the distillation zone or the isomerization zone.

Acidic catalysts are used for the isomerization of the 2-butenes to 1-butene, and these catalysts can be employed in the liquid phase, for example as aqueous

mineral acids, preferably aqueous phosphoric acids, for example phosphoric acids containing from 1 to 80, preferably from 2 to 75, % by weight of P_2O_5 , or as solid catalysts.

- 5 Advantageous solid acidic catalysts are solid phosphoric acid catalysts which contain monophosphoric acid or, preferably, polyphosphoric acid on a solid carrier. Examples of suitable carriers for the phosphoric acid catalysts are alumina, silica, active carbon, kiesel-
10 guhr or pumice. Preferably, silica gel is used as a carrier.

- Other suitable acidic catalysts are acidic metal sulfates, such as sodium bisulfate, calcium bisulfate, aluminum sulfates, nickel sulfate, copper sulfate, cobalt
15 sulfate, cadmium sulfate or strontium sulfate. These acidic metal sulfates can be used as such but are preferably employed on a carrier. Examples of suitable carriers are silica gel, active carbon, alumina and pumice.

- Silica gel or alumina alone and advantageously
20 zeolites can also be used as catalysts for the isomerization. Particularly advantageously used catalysts are borosilicate or aluminosilicate zeolites of the pentasil type.

- The zeolite catalysts can be modified in various
25 ways to increase the selectivity, the life and the number of times the catalysts can be regenerated.

- In one method of modification, the unmolded or
molded zeolites are subjected to ion exchange, or are doped, with alkali metals, such as Na, alkaline earth
30 metals, such as Ca or Mg, earth metals, such as B or Tl, transition metals, such as Mn, Fe, Mo, Cu or Zn, and/or rare earth metals, such as La or Ce. In an embodiment of this method of modification, for example, the molded pentasil zeolites are initially taken in a siphon tube,
35 and a salt of one of the above metals, eg. a halide or a nitrate, is passed over at room temperature or elevated temperatures, for example from 20 to 120°C, preferably

from 20 to 100°C. This type of ion exchange can be carried out on, for example, the hydrogen, ammonium or alkali metal form of the zeolite. In another embodiment of the method of modification, the zeolite material is
5 impregnated with compounds of the above metals, for example the halide, nitrate and/or oxide, in a liquid medium, for example in aqueous or alcoholic solution. Ion exchange as well as impregnation are advantageously followed by drying and/or calcination. In the case of the
10 metal-doped zeolites, it may be advantageous to follow the stages with an after-treatment with hydrogen.

In another possible method of modification, the unmolded or molded zeolite material is treated with an acid, such as hydrochloric acid, hydrofluoric acid or phosphoric
15 acid. In a particular embodiment of the acid treatment, the zeolite material, before being molded, is treated, at elevated temperatures, with hydrofluoric acid, in general 0.001 - 2 N, preferably 0.05 - 0.5 N, hydrofluoric acid, for example by refluxing for in general from 0.5 to 5, preferably from 1 to 3, hours. The zeolite material is isolated, for example by filtering it off and washing it, and is then advantageously dried, for example at from 100 to 160°C, and calcined at in general from 450 to 600°C. In another
20 preferred embodiment of the acid treatment, the zeolite material is first molded with a binder and then treated with hydrochloric acid, in general from 3 to 25, preferably from 12 to 20, % strength by weight hydrochloric acid, at elevated temperatures, advantageously at from 50 to 90°C, preferably from 60 to 80°C, for from 0.5 to 5, preferably from 1
25 to 3, hours. The zeolite material is then generally washed and is advantageously dried, for example at from 100 to 160°C, and calcined at in general from 450 to 600°C.

In another embodiment of the novel process, the acidic catalyst used for the isomerization is a metal
35 phosphate, in particular a metal hydrogen phosphate. These phosphates may also contain an excess of phosphoric acid over and above the stoichiometric composition of the

acidic metal phosphates, for example an excess as high as 65%, preferably as high as 20%, in particular as high as 10%. Examples of suitable metal phosphates of this type are magnesium phosphate, calcium phosphates, strontium phosphates, barium phosphates, manganese phosphates, nickel phosphates, copper phosphates, cobalt phosphates, cadmium phosphates, iron(II) phosphates, chromium phosphates and in particular aluminum phosphates. The metal phosphate catalyst can be used as such or on a carrier, examples of suitable carriers being alumina, silica, active carbon and zinc oxide.

The amount of acidic catalyst is generally about 0.01 - 10, preferably about 0.03 - 2, kg per kg/hour of 2-butenes which are to be isomerized and which are passed through the reactor. A fixed-bed reactor is preferably used for the isomerization.

When the activity of the solid acidic catalyst diminishes, the catalyst is advantageously regenerated. In an advantageous method for regenerating the solid catalyst, the latter is treated with phosphoric acid, advantageously with aqueous phosphoric acid. This treatment can be carried out continuously, ie. without interrupting the isomerization reaction, this advantageously being done by introducing aqueous phosphoric acid onto the catalyst at the isomerization temperature during the isomerization. In general, the phosphoric acid is added in an amount such that from 10^{-6} to 10^{-3} , preferably from 10^{-5} to 10^{-4} , kg/hour of P_2O_5 is added per kg of catalyst. The regeneration of the solid catalyst can also be carried out batchwise, ie. with interruption of the isomerization reaction. Batchwise isomerization is also advantageously carried out at elevated temperatures, for example at from 50 to 300°C, preferably from 50 to 250°C, in particular from 50 to 150°C, and the phosphoric acid is generally introduced onto the catalyst in an amount such that about 0.1 - 20% by weight, based on the catalyst, of P_2O_5 is added. In general, the treatment of the solid catalyst

with phosphoric acid is carried out by allowing the latter, advantageously in the form of aqueous phosphoric acid, to trickle over the catalyst.

In another advantageous method, the solid acidic catalyst can be regenerated by combustion with an oxygen-containing gas, preferably air. It may be advantageous to dilute the air with an inert gas, eg. nitrogen. The treatment of the catalyst with the oxygen-containing gas is generally carried out at from 300 to 500°C.

The isomerization of the 2-butenes to 1-butene in the isomerization zone is carried out at from 150 to 500°C, preferably from 200 to 450°C, in particular from 250 to 400°C, under atmospheric pressure but preferably under superatmospheric pressure, advantageously under a pressure as high as 100 bar. Where solid catalysts are used, the pressure employed is preferably from 2 to 60, in particular from 6 to 40, bar, and where liquid catalysts are used, the pressure employed is preferably from 10 to 100, in particular from 30 to 50, bar.

An advantage of the novel process is that there is no need to add steam to the 2-butene-containing C₄-hydrocarbon mixture passed into the isomerization zone. Although it is also possible for the C₄-hydrocarbon mixture being isomerized to be diluted with steam, the amount of steam added to this mixture is as a rule restricted to less than 1, preferably not more than 0.8, in particular not more than 0.5, mole of water per mole of 2-butenes.

To separate off the 1-butene from the 2-butenes, the isomerization mixture obtained from the isomerization zone is then passed into a distillation zone, in which the 1-butene is advantageously taken off as a top product by conventional distillation. The distillation is generally carried out using a conventional distillation column containing, for example, about 100 trays.

A fraction containing 2-butenes is taken off in the lower third of the distillation zone and recycled into the isomerization zone. In a preferred embodiment of the

process according to the invention, the 2-butene-containing fraction removed from the lower third of the distillation zone contains from 1 to 15, preferably from 1 to 12, in particular from 2 to 10, % by weight of 1-butene.

- 5 Surprisingly, when this relatively high content of 1-butene is established in the fraction recycled from the lower third of the distillation zone into the isomerization zone, the specific energy requirement of the novel process is reduced, chiefly because this recycling of 1-
- 10 butene to the isomerization zone reduces the difference between the concentration of 1-butene in the recycled butene fraction and the 1-butene concentration corresponding to the equilibrium in the isomerization zone.

In the Figure, an embodiment of the novel process

15 is illustrated diagrammatically by way of example. The starting C_4 -hydrocarbon mixture which contains 2-butenes and may or may not contain 1-butene is fed to distillation column 3 through line 1, and/or directly to the isomerization reactor 5 through lines 2 and 4. A fraction contain-

20 ing butenes is taken off at the bottom of the distillation column and is fed via line 4 to the isomerization reactor, in which the 2-butenes are isomerized to 1-butene over an acidic catalyst. The isomerization mixture is removed from the isomerization reactor via line 6 and is fed to the distillation column, advantageously into the lower half of

25 this column, the sensible heat of the isomerization mixture advantageously being used in the reboiler 7 for reboiling in the distillation column. However, heat exchange with the butene-containing fraction fed to the isomerization reactor via line 4 can also be carried out. The 1-

30 butene taken off at the top of the distillation column via line 8 is very pure and as a rule can be processed further without additional purification operations.

- 35 1-Butene is an important starting material, for example for the preparation of polymers, such as polybut-1-ene, or copolymers, for example with ethene, for the preparation of linear low density polyethylene (LDPE), and

for the preparation of butene oxide.

The Example which follows illustrates the invention.

EXAMPLE

- 5 For the recovery of 1-butene, a starting C₄-hydrocarbon mixture of the following composition was used:
- | | |
|----------------|-----------------|
| trans-2-butene | 24.4% by weight |
| cis-2-butene | 19.8% by weight |
| 1-butene | 55.8% by weight |
| 10 butanes | traces |

- This mixture of butenes was obtained as follows: first, the butadiene was extracted, by means of extractive distillation, from a C₄ fraction obtained from an ethylene plant, isobutene was separated off in a further stage,
- 15 methyl tert.-butyl ether being obtained, and finally the butanes were separated off by means of a further extractive distillation.

- 100 g/hour of the butene mixture of the composition stated above were passed into the middle third of a
- 20 distillation column. 825 g/hour of a bottom fraction consisting of 95% by weight of 2-butenes and 5% by weight of 1-butene were taken off at the bottom of the distillation column and passed into an isomerization reactor which contained a fixed-bed phosphoric acid/silica gel catalyst
- 25 and in which a reaction temperature of from 250 to 300°C was maintained. The isomerization mixture removed from this reactor and consisting of 90% by weight of 2-butenes and 10% by weight of 1-butene was passed into the lower third of the distillation column. 100 g/hour of 1-butene
- 30 having a purity of 99.5% by weight were taken off at the top of the distillation column. The yield of 1-butene was 178%, based on the 1-butene present in the starting C₄-hydrocarbon mixture.

- Traces of C₈-hydrocarbons formed from the mixture
- 35 used in the isomerization, as well as small amounts of butane, could be separated off by recycling some of the bottom fraction from the distillation column to the up-

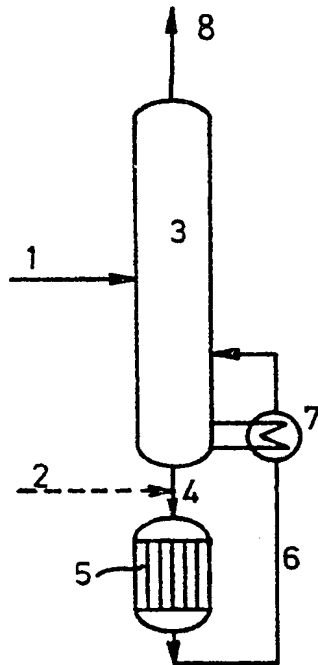
stream extractive distillation.

By means of the recycling procedure, the n-butenes could be converted virtually completely to 1-butene.

When the conversion in the isomerization decreased,
5 the following measures were taken:

1. Steam was added to the mixture of 2-butenes and 1-butene which was fed to the isomerization reactor.
2. The isomerization catalyst was regenerated by treating it with aqueous phosphoric acid.
- 10 3. The isomerization catalyst was regenerated by treating it with a mixture of air and nitrogen at 400°C.

While the addition of steam (measure 1) had no detectable effect, regeneration of the isomerization catalyst according to measure 2 or 3 had the result that the
15 conversion once again corresponded to the initial conversion over the fresh catalyst.



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